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(54) Title: NANOPARTICLE-BASED PERMANENT TREATMENTS FOR TEXTILES

(57) Abstract: This invention is directed to preparations useful for the permanent or substantially permanent treatment of textiles and other webs. More particularly, the preparations of the invention comprise an agent or other payload surrounded by or contained within a synthetic, polymer shell or matrix that is reactive to webs, to give textile-reactive beads or matrices. By "textile-reactive" is meant that the payload bead will form a chemical covalent bond with the fiber, yarn, fabric, textile, finished goods (including apparel), or other web or substrate to be treated. The polymer shell or polymer network of the payload nanoparticle has a surface that includes functional groups for binding or attachment to the fibers of the textiles or other webs to be treated, to provide permanent attachment of the payload to the textiles. Alternatively, the surface of the nanobead includes functional groups that can bind to a linker molecule that will in turn bind or attach the bead to the fiber.

NANOPARTICLE-BASED PERMANENT TREATMENTS FOR TEXTILES

FIELD OF THE INVENTION

5 This invention is directed to the field of fabric and textile treatments. More specifically, this invention relates to preparations and their use in providing substantially permanent desirable characteristics to textiles.

BACKGROUND OF THE INVENTION

10 Fabric treatments endowing particular characteristics or activity are highly desired by the apparel, home furnishings, and medical industries. However, conventional processes used to impart such characteristics often do not lead to permanent effects. Laundering or wearing of the treated fabric causes leaching or erosion of the agents responsible for imparting the desired characteristics. This deficiency has resulted in research efforts to develop durable
15 treatments. Chemical bonding of the compounds onto the fabrics enhances their durability. Unfortunately, the required chemical modifications often cause concomitant reduction or loss of activity or other desired characteristics and must be individually developed for the different agents on a case-by-case basis. Labile or hydrolyzable linkers for direct chemical attachment or controlled release are difficult to engineer and must be individually developed for the
20 different agents on a case-by-case basis. Yet, their decomposition kinetics are generally difficult to control.

There is thus a need for a robust and precisely controllable methodology for, fiber, yarn, fabric, and/or textile (web) treatment with agents to provide stability and permanence to, without impairing the desired characteristics of, the agent. Furthermore, for certain situations,
25 there is a need to controllably release the agents over a prolonged duration (e.g., fragrances, biocides, anti-fungals, etc.).

SUMMARY OF THE INVENTION

This invention is directed to preparations useful for the permanent or substantially
30 permanent treatment of various types of textile materials and other substrates and webs. More particularly, the preparations of the invention comprise an agent or other payload entrapped, that is, surrounded by or contained within a synthetic, polymer shell or matrix that is reactive to fibers, yarns, fabrics, or webs, to give textile-reactive beads or matrices. The beads or matrices are micrometric or nanometric in size, and are herein collectively and interchangeably referred to as "nanobeads" and "nanoparticles". The nanobead/nanoparticle of the invention
35 may comprise a polymeric shell surrounding the payload or it may comprise a three-dimensional polymeric network entrapping the payload, both of which are referred to herein as

a "polymer shell". By "textile-reactive" is meant that the payload bead will form a chemical covalent bond with the fiber, yarn, fabric, textile, finished goods (including apparel), or other web or substrate to be treated.

The polymer shell or polymer network of the payload nanoparticle has a surface that includes functional groups for binding or attachment to the fibers, filaments or structural components or elements (referred to collectively herein and in the appended claims as "fibers") of the textiles or other webs to be treated, to provide permanent attachment of the payload to the fibers. Alternatively, the surface of the nanobead includes functional groups that can bind to a linker molecule that will in turn bind or attach the bead to the fiber. In either case, these functional groups are referred to herein as "textile-reactive functional groups" or "fiber-reactive functional groups" or "substrate-reactive functional groups".

The terms "payload" and "payload agent" as used herein refer collectively to any material or agent that would be desirable for permanent attachment to or treatment of a textile or other web. Alternatively, the payload agent may be released from the cage of the payload nanobead in a controlled and prolonged fashion.

The chemical linkage on the surface of the nanobead does not involve the molecules of the payload. The payload agents are physically entrapped within the nanoparticle, thus requiring no chemical modifications of the agents themselves. The resulting encapsulated payload preparations or nanoparticles have improved retention within and on the textile or web fiber structure without changing the inherent character of the payload agent.

The architecture of the shell or matrix of the nanobead can be formulated and fine-tuned to exhibit controlled release of the entrapped payload, ranging from constant but prolonged release (desirable for drugs, biologic or anti-biologic agents, softeners, and fragrances, for example) to zero release (desirable for dyes, metallic reflector colloids, and sunblock agents, for example). In an encapsulated configuration, the beads will desirably insulate the payload from the skin, preventing potential allergic reactions. In addition, the nanoparticle can be designed to respond to different environmental stimuli (such as temperature, light change, pH, or moisture) to increase the rate of release, color change, or temperature change at certain times or in certain selected spots or locations on the textile or finished good.

This invention is further directed to the fibers, yarns, fabrics (which may be woven, knitted, stitch-bonded or nonwoven), other textiles, or finished goods (encompassed collectively herein under the terms "textiles" or "webs") treated with the textile-reactive nanoparticles. Such textiles and webs exhibit a greatly improved retention or durability of the payload agent and its activity, even after multiple washings.

Methods are provided for synthesizing a textile-reactive payload-containing nanoparticle. The preparations of the invention may be formed via one of several methods of

encapsulation, such as interfacial polymerization, microemulsion polymerization, precipitation polymerization, and diffusion. Multi-component mixture preparation followed by atomization/spraying into a drying chamber is yet another processing scheme. Reactive functional groups on the polymer shell provide a means for attaching the payload nanoparticles to textiles.

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DETAILED DESCRIPTION OF THE INVENTION

The textile-reactive preparations of the invention comprise an agent or payload surrounded by or contained within a synthetic, polymer shell or matrix that is reactive to textiles or other webs, to give textile-reactive payload nanoparticles. The polymer shell or matrix of the nanoparticle has a surface that includes functional groups for binding or attachment to the fibers of the textiles or other webs to be treated.

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The terms "payload" and "payload agent" as used herein refer collectively to any material or agent that would be desirable for permanent or semi-permanent attachment to or treatment of a textile or other web. The payload may include, but is not limited to, bioactive or anti-biologic agents, drugs and pharmaceuticals, sunblock agents, dyes (such as iridescent dyes, fixed dyes, and dyes that respond to a particular environmental or chemical trigger such as heat, pH, carbon monoxide, sulfuric acid, or minute quantities of blood, for example), pigments, scents and fragrances, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, thermochromic materials, insect repellents, heat-absorbing or -releasing phase change agents, fabric softeners, zeolites and activated carbon (useful for absorbing environmental hazards such as toxins and chemicals including formaldehyde), and the like. While the following discussions herein are directed to certain exemplary agents, it is important to note that other materials having any desirable activity suitable for textile treatments may also be encapsulated according to the teachings herein and are included within the scope of this invention.

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The nanoparticles of the invention are formed by contacting an agent or other payload with a set of monomers, oligomers, or polymers (referred to herein as a "polymeric set"). The monomers, oligomers, or polymers assemble around the payload and then are polymerized, with or without crosslinking, into a polymeric network or shell surrounding the payload agent. The polymeric set includes at least some components that provide reactive "hooks" or functional groups on the surface of the final polymeric bead, which will bind to the textile structural members or web fibers to be treated.

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Alternatively, a bead having functional groups on its surface can first be prepared by polymerizing a polymeric set, after which a payload can be exposed to the bead under suitable conditions such that the payload is absorbed into and entrapped in the polymeric network, to provide the textile-reactive payload nanobead of the invention.

Particular monomers, oligomers, or polymers useful in forming the nanoparticles of the present invention are those that contain amine, hydroxyl, or sulfhydryl monomers or polymers combined with amine-, hydroxyl-, or sulfhydryl-reactive monomers or polymers. Specific examples include, but are not limited to, monomers or polymers of maleic anhydride and a di-
5 or polyamine (monomer or polymer). Presently preferred monomers are anhydrides. Other free-radical polymerizable reactive groups that can be used are acrylates, methacrylates, alkenes, acrylamides, etc. Examples of hydrophilic and hydrophobic monomers are listed below. Many of these monomers are commercially available, for example from Polysciences, Inc., Warrington, PA.

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Hydrophobic Monomers

- N-(*tert*-Butyl)acrylamide
- n-Decyl acrylamide
- n-Decyl methacrylate
- 15 N-Dodecylmethacrylamide
- 2-Ethylhexyl acrylate
- 1-Hexadecyl methacrylate
- n-Myristyl acrylate
- 20 N-(n-Octadecyl) acrylamide
- n-Octadecyltriethoxsilane
- N-*tert*-Octylacrylate
- Stearyl acrylate
- 25 Stearyl methacrylate
- Vinyl laurate
- Vinyl stearate

Hydrophobic Monomers - Fluorinated

- 1H,1H,7H-Dodecafluoroheptyl methacrylate
- 2-Fluorostyrene
- 30 4-Fluorostyrene
- 1H,1H,2H,2H-Heptadecafluorodecyl acrylate
- 1H,1H,2H,2H-Heptadecafluorodecyl methacrylate
- 1H,1H-Heptafluorobutyl acrylate
- 1H,1H-Heptafluorobutyl methacrylate
- 35 1H,1H,4H-Hexafluorobutyl acrylate
- 1H,1H,4H-Hexafluorobutyl methacrylate
- Hexafluoro-iso-propyl acrylate
- Methacryloyl fluoride
- 1H,1H-Pentadecafluoroctyl acrylate
- 40 1H,1H-Pentadecafluoroctyl methacrylate
- Pentafluorophenyl acrylate
- Pentafluorophenyl methacrylate
- 2,3,4,5,6-Pentafluorostyrene
- 1H,1H,3H-Tetrafluoropropyl acrylate
- 45 1H,1H,3H-Tetrafluoropropyl methacrylate
- 2,2,2-Trifluoroethyl acrylate
- 2,2,2-Trifluoroethyl methacrylate

Hydrophilic Monomers

5 Acrylamide
 Acrylic acid
 N-Acryloyltris(hydroxymethyl)methylamine
 Bisacrylamidoacetic acid
 Glycerol mono(meth)acrylate
 4-Hydroxybutyl methacrylate
 2-Hydroxyethyl acrylate
 2-Hydroxyethyl methacrylate (glycol methacrylate)
10 N-(2-Hydroxypropyl)methacrylamide
 N-Methacryloyltris(hydroxymethyl)methylamine
 N-Methylmethacrylamide
 Poly(ethylene glycol) (n) monomethacrylate
 Poly(ethylene glycol) (n) monomethyl ether monomethacrylate
15 2-Sulfoethyl methacrylate
 1,1,1-Trimethylolpropane monoallyl ether
 N-Vinyl-2-pyrrolidone (1-vinyl-2-pyrrolidinone)

20 The monomers, oligomers, or polymers may optionally be copolymerized with acrylated or methacrylated soft or rubbery (elastomeric) monomers or polymers to impregnate and thereby increase the durable press properties of the fabric, to add to the softness, and/or to aid in the resistance to abrasive wear. The rubbery groups are selected from those groups that will provide the necessary degree of wrinkle resistance, softness, durability, strength, and abrasion resistance. Examples include polymers of isoprene, chloroprene, and polymers such
25 as polydimethylsiloxane, polyisobutylene, poly-alt-styrene-co-butadiene, poly-random-styrene-co-butadiene, polyethylene glycol, polypropylene glycol, etc., and copolymers of all of these.

30 The textile-reactive hooks or functional groups on the surface of the textile-reactive nanoparticles are selected from those groups that will bind chemically with a particular structural element, fiber, yarn, fabric, or finished good. For example, cellulosic-based webs (such as paper, cotton, rayon and other regenerated cellulosics and cellulose-containing materials such as Tencel® and Lyocell, as well as linen, jute, ramie and industrial hemp or the like) contain hydroxyls. Wool, which is a proteinaceous animal fiber, as well as silk and regenerated proteins, and other animal fibers contain hydroxyls, amines, carboxylates, and thiols (disulfides). The textile-reactive hooks may contain carboxyl groups in close proximity to each other so that they can be re-formed into a reactive anhydride by a catalyst when the catalyst and the textile-reactive beads are heated in the presence of a material that contains hydroxyls or amines (such as, for example, cotton or wool). Alternatively, the hooks may contain epoxide groups or other groups, such as halohydrins, that can be converted to epoxy groups. Also, methylolacrylamide (methylol groups are known to react with cotton, e.g.
35 DMDHEU) may be copolymerized into the bead matrix. Anhydride groups are presently preferred.
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Specific amine-reactive groups (for reaction with wool, for example) include isothiocyanates, isocyanates, acyl azides, N-hydroxysuccinimide esters, sulfonyl chlorides, aldehydes and glyoxals, epoxides and oxiranes, carbonates, arylating agents, imidoesters, carbodiimides, anhydrides (such as maleic anhydride), and halohydrins. Carboxylate-reactive groups (for reaction with wool, e.g.) include diazoalkanes and diazoacetyl compounds, carbonyl diimidazole, and carbodiimides. Hydroxyl-reactive chemical reactions (for, e.g., wool and cotton) include epoxides and oxiranes, carbonyl diimidazole, N,N'-disuccinimidyl carbonate or N-hydroxysuccinimidyl chloroformate, oxidation with periodate, enzymatic oxidazation, alkyl halogens, isocyanates, and halohydrins. Examples of thiol-reactive chemical reactions (for wool, for example) are haloacetyl and alkyl halide derivatives, maleimides, aziridines, acryloyl derivatives, arylating agents, and thiol-disulfide exchange reagents (such as pyridyl disulfides, disulfide reductants, and 5-thio-2-nitrobenzoic acid).

Alternatively, the payload nanobead has surface functional groups that will react with a molecule, which molecule will then attach to the fiber or textile to be treated, acting as a linker between the textile and the payload nanobead. Thus, for example, in one embodiment of the invention, the encapsulated payload beads are attached via their surface functional groups to an N-methylol resin compound and the N-methylol compound is covalently attached to the textile or web. The N-methylol-containing compound thus acts as an attachment bridge or linker between the payload bead and the textile. In the practice of the invention, the N-methylol compound may react first with either the fabric or the payload bead. An additional advantage is that the N-methylol-containing compound, when present in an appropriate amount (the manufacturer recommends 8 wt% for DMDHEU), will provide a durable press finish to the final payload-treated textile or web.

Where it is desirable for a controlled release of the payload on or into the textile, the textile-reactive payload nanoparticle of the invention is designed so that the payload agent is embedded or entrapped within the polymeric shell or matrix of the nanoparticle but is also able to be released from the nanoparticle in a prolonged or otherwise controllable fashion. The release profile is programmed via the chemistry of the polymer network of the nanobead. The nanobead or nanoparticle can be formulated with an almost infinite degree of designed characteristics via key structural features, such as crosslinking density, hydrophilic-hydrophobic balance of the copolymer repeat units, and the stiffness/elasticity of the polymer network (for example, the glass transition temperature). In addition, erodible nanobeads can be developed to encompass dual release mechanisms of diffusion and erosion.

Furthermore, the polymer matrix may contain components that react or respond to environmental stimuli to cause increased/decreased content release. "Smart polymers" are polymers that can be induced to undergo a distinct thermodynamic transition by the adjustment of any of a number of environmental parameters (e.g., pH, temperature, ionic strength, co-

solvent composition, pressure, electric field, etc.). For example, smart polymers based on the lower critical solution temperature (LCST) transition may drastically cut off release when exposed to hot water during laundering. When cooled back to room temperature, sustained release resumes. Smart polymers may be selected from, but are not limited to, N-isopropyl acrylamide and acrylamide; polyethylene glycol, di-acrylate and hydroxyethylmethacrylate; octyl/decyl acrylate; acylated aromatic and urethane oligomers; vinylsilicones and silicone acrylate; polypropylene glycols, polyvinylmethyl ether; polyvinylethyl ether; polyvinyl alcohol; polyvinyl acetate; polyvinyl pyrrolidone; polyhydroxypropyl acrylate; ethylene, acrylate and methylmethacrylate; nonyl phenol; cellulose; methyl cellulose; hydroxyethyl cellulose; hydroxypropyl methyl cellulose; hydroxypropyl cellulose; ethyl hydroxyethyl cellulose; hydrophobically-modified cellulose; dextran; hydrophobically-modified dextran; agarose; low-gelling-temperature agarose; and copolymers thereof. If crosslinking is desired between the polymers, multifunctional compounds such as bis-acrylamide and ethoxylated trimethylol propane triacrylate and sulfonated styrene may be employed. In presently preferred embodiments, the smart polymers comprise polyacrylamides, substituted polyacrylamides, polyvinylmethyl ethers, and modified celluloses.

Where it is desirable for the payload to be visible (when it is a dye, a UV protector, or a metallic reflector, for example), the nanobead will be constructed of optically transparent or translucent material, allowing light to come into contact with the payload and be reflected, refracted or absorbed.

The polymeric set can be chosen to give either hydrophobic or oleophilic nanoparticles, allowing a wider array of bioactive compounds or drugs to be comfortably entrapped within. Where the particles are hydrophilic, they are easily dispersible in a stable aqueous suspension or emulsion by surfactants, which can subsequently be washed away without affecting the performance of the payload agent within. The inherent thermodynamic compatibility of the agents and the polymeric shell or matrix material can increase the loading level per particle.

The textile-reactive payload nanoparticles of the invention are present in their final form as beads or particles having a diameter of from a few microns to a few nanometers, preferably from about 1 to about 1000 nm, more preferably from about 10 to about 500 nm. The size of the textile-reactive nanoparticles or nanobeads will primarily be chosen for the best penetration into the particular fiber to be treated. Additionally, the particles can be engineered to have either a narrow or a broad size distribution, depending on the intended release profile of the active agent.

The textile-reactive nanoparticles of the present invention can be formed in one of several ways, with the exact procedure for bead or particle formation being determined by features such as solubility of the payload agent and/or the monomers/oligomers/polymers of the polymeric set; light, heat, or mechanical stability; and the like. Additional considerations,

such as the desired properties of the resulting textile-reactive nanoparticle, as well as the choice of fiber to which it is intended to be bound, may also dictate the exact formulation procedure required. Generally, to form the textile-reactive payload nanoparticle, the target payload agent is dissolved in a suitable solvent (or alternatively, if the agent is a particulate, it is suspended in a suitable medium), and a polymeric set (that is, a set of monomers, oligomers, or polymers, including appropriate textile-reactive hooks or functional groups) is added. The polymeric set (i.e., the monomers, oligomers, or polymers) is then subsequently polymerized, giving the textile-reactive payload nanoparticle.

In one present embodiment of the invention, where the payload agent is soluble in water, the polymeric set and the water-soluble agent are dispersed in an aqueous medium, to which is then added an organic compound and an emulsifier, such that the aqueous phase forms a fine emulsion (which comprises microspheres of the payload agent and the monomers/oligomers/polymers) in the continuous organic phase. An oil-soluble polymer or other compound having an excess of textile-reactive functional groups and monomer-reactive functional groups is added to the aqueous phase. The oil-soluble compound crosslinks with the monomers, oligomers, or polymers to form a polymer shell around the aqueous microspheres, encapsulating the payload agent and having uncrosslinked textile-reactive functional groups on the polymer surface capable of attachment to the fibers of a textile or web to be treated, to give a textile-reactive payload nanobead.

In the above method, a presently preferred oil-soluble polymer is poly(maleic anhydride) or poly(styrene-co-maleic anhydride).

Where a particular payload agent is water-insoluble (such as indigo dye, for example), it may be converted to a water-soluble form (to leuco indigo, in the case of indigo) prior to reaction with the monomers, oligomers, or polymers and the oil-soluble compound following the above method. After the bead formation is completed, the payload is converted back to its water-insoluble form within the bead (by oxidation of leuco indigo, in the case of indigo).

In another embodiment of the invention, a water-insoluble payload agent is dissolved in an organic solution with a polymer that includes an excess of textile-reactive functional groups. The organic solution containing the payload agent is added to an aqueous medium containing a set of monomers, oligomers, or polymers reactive with the first, oil-soluble polymer to permit some of the functional groups to crosslink with the monomers to form a polymer shell around particles of the agent. The resulting textile-reactive payload nanoparticle encapsulates the payload agent and has uncrosslinked textile-reactive functional groups on its polymer surface capable of attachment to the fibers of a textile or web to be treated.

In the above method, a presently preferred oil-soluble polymer is styrene-maleic anhydride copolymer.

In a third embodiment of a method (bead swelling) according to the invention, a polymer bead having textile-reactive functional groups on its surface is made, following procedures known in the art. This bead is then placed into a solvent that causes the bead to swell, opening pores or passages in the wall of the bead. A payload agent is placed in the solvent together with the polymer bead; the agent will diffuse into the swelled bead. The swollen bead containing the payload agent is then treated with a second solvent to collapse the wall of the bead, to give a textile-reactive nanobead entrapping a payload agent.

The polymeric nanobeads of the invention may also be prepared by atomization. A solution of the bead-forming polymer is formed from a polymeric set with a suitable solvent, and the payload is added to the solvated polymer. If the payload is a solid, it may either be solubilized in the solvent or, if it is insoluble in the solvent, it should be of a sufficiently small size and well dispersed in the polymeric solution. The polymer solution is then atomized into a drying gas atmosphere where solvent removal proceeds by simple evaporative drying. Such atomization techniques include, for example, high-pressure atomization, two-fluid atomization, rotary atomization, and ultrasonic atomization. The type of technique used, as well as the operating parameters, will depend on the desired particle or bead size distribution and the composition of the solution being sprayed. Such techniques are well taught in the literature, and ample description can be found in many texts such as, for example, *Spray Drying Handbook* by K. Masters, herein incorporated by reference.

Droplet formation may be alternatively accomplished by introducing the polymer solvent solution into a second, immiscible liquid in which the polymer and payload agent are immiscible and the polymer solvent is only slightly soluble. With agitation the polymer solution will break up into finely dispersed droplets, forming a suspension of spherical polymer solution droplets distributed within the second liquid. The second liquid shall be chosen such that it is not a solvent for the polymer, and is somewhat incompatible with the polymer solvent such that the overall polymer solution is dispersible as discrete droplets with the second liquid. The second liquid must, however, provide a reasonable solubility for the polymer solvent such that the polymer solvent is extracted from the microdroplets in a manner analogous to evaporative drying. That is, as the microdroplets make contact with and disperse in the second, immiscible liquid, the polymer solvent is extracted from the droplets at their surfaces. Once sufficient solvent has been removed, the polymer will phase separate and form a polymer shell at the droplet surface, as in the case of evaporative drying. Further extraction of the solvent through the polymer shell wall results in nanobeads or nanoparticles composed of a polymer shell wall surrounding the payload agent.

In forming the textile-reactive nanoparticles or nanobeads, additional crosslinkers or complementary reactive functionalities may also be added to the solution to help create bridges between crosslinkable groups and to alter the crosslink density. Polymerization can be

accomplished by reaction methods known in the art. The crosslinking of the monomers, oligomers, or polymers and the textile-reactive functional groups can be generated, for example, by heat or by radiation, such as UV light or gamma rays. Catalysts or photo- or thermal-initiators can be used to promote crosslinking. Such initiators and catalysts are 5 commercially available.

In preparing the textile-reactive nanoparticles of the invention, the process temperature can vary widely, depending on the reactivity of the reactants. However, the temperature should not be so high as to decompose the reactants or so low as to cause inhibition of the reaction or freezing of the solvent. Unless specified to the contrary, the processes described 10 herein take place at atmospheric pressure over a temperature range from about 5°C to about 150°C, more preferably from about 10°C to about 100°C, and most preferably at "room" or "ambient" temperature ("RT"), e.g. about 20°C. The time required for the processes herein will depend to a large extent on the temperature being used and the relative reactivities of the starting materials. Following formation, the textile-reactive payload nanoparticles can be 15 isolated by filtration, by gravity/settling/floating, by centrifugation, or by evaporation, for example, or by other known techniques. Any residual oil can be removed, if desired, by extraction with an appropriate solvent, by distillation at reduced pressure, or by other known techniques. Unless otherwise specified, the process times and conditions are intended to be approximate. Those skilled in the art of polymerization reaction engineering and materials 20 handling engineering can readily devise the appropriate processes for the intended applications.

This invention is further directed to the fibers, yarns, fabrics, textiles, or finished goods (encompassed herein under the terms "textiles" and "webs") treated with the textile-reactive nanoparticles. Such textiles or webs exhibit a greatly improved retention of the payload and its 25 activity, even after multiple washings. For example, where the payload is a dye, the treated textiles or webs exhibit a greatly improved colorfastness and resistance to fading. Textiles or webs treated with beads containing a sunblock agent as the payload will absorb, block, reflect or otherwise prevent or substantially prevent harmful UV radiation from passing through the textile and also will not harm the textile itself. When the payload is an anti-biologic agent, a drug, a pharmaceutical or an enzyme, e.g., because of the durability of the chemical bonds 30 between the fibers and the functional groups of the nanoparticles, the bioactive agents are depleted only by programmed release from the particles and not from unintended detachment or release of the particles themselves from the web.

The novel webs of the present invention include fibers and/or filaments; woven, knitted, 35 stitchbonded, and non-woven fabrics derived from natural, man made, and/or synthetic fibers and blends of such fibers; cellulose-based papers; and the like. They can comprise fibers in the form of continuous or discontinuous monofilaments, multifilaments, fibrils, fibrillated tapes

or films, staple fibers, and yarns containing such filaments and/or fibers, and the like, which fibers can be of any desired composition. The fibers can be of natural, man made, or synthetic origin. Mixtures of natural fibers, man-made fibers, and synthetic fibers can also be used. Included with the fibers can be non-fibrous elements, such as particulate fillers, flock, binders, sizes and the like. The textiles and webs of the invention are intended to include fabrics and textiles, and may be a sheet-like structure [woven (including jacquard woven for home furnishings fabrics) or non-woven, knitted (including weft inserted warp knits), tufted, or stitch bonded] and may be comprised of any of a variety of fibers or structural elements. The nonwovens may be stitch bonded, ultrasonic bonded, wet laid, dry laid, solvent extruded, air or gas blown, jet interlaced, hydroentangled, and the like, and may have a broad variety of properties including stretch, air permeability, or water vapor breathability. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of manmade fibers derived primarily from natural sources include regenerated cellulose rayon, Tencel® and Lyocell, cellulose esters such as cellulose acetate, cellulose triacetate, and regenerated proteins.

Examples of synthetic fibers or structural elements include polyesters (including polyethyleneglycol terephthalate), wholly synthetic polyesters, polyesters derived from natural or biologic materials such as corn, polyamides (including nylon, such as nylon 6 and 6,6), acrylics, olefins such as polyethylene or polypropylene, aramids, azlons, modacrylics, novoloids, nitrils, aramids, spandex, vinyl polymers and copolymers, vinal, vinyon, and the like, and hybrids of such fibers and polymers.

To prepare webs having a permanently attached payload, the fiber, the yarn, the fabric, or the finished good is exposed to a solution or dispersion/emulsion of the textile-reactive payload nanoparticles, by methods known in the art such as by soaking, spraying, dipping, fluid-flow, padding, and the like. If needed for the reaction, a catalyst is also present in the medium. The textile-reactive functional groups on the nanoparticles react with the textile or web, by covalent bonding, to permanently attach to the textile. This curing can take place either before or after the treated textile is removed from the solution and dried, although it is generally preferred that the cure occur after the drying step.

Alternatively, textile-reactive payload beads are suspended in an aqueous solution that contains a compound having two or more N-methylol groups, such as DMDHEU or DMUG, and a Lewis acid catalyst, such as MgCl₂. A surfactant may be used to help suspend the particles. The fiber, the yarn, the fabric, the nonwoven web, or the finished good to be treated is then exposed to the solution containing the textile-reactive payload beads and the N-methylol-containing compounds, by methods known in the art such as by soaking, spraying, dipping, fluid-flow, padding, and the like. The N-methylol groups react with the web, by covalent bonding, and the functional groups on the payload-laden beads react with the N-

methylol-containing compounds to permanently attach the beads to the web. The treated web is then removed from the solution and dried.

The concentration of the textile-reactive payload nanoparticles in solution can be from about 0.1% to about 95%, preferably from about 0.75% to about 75%, more preferably from about 1% to about 50%; depending, however, on the rheological characteristics of the particular polymer nanoparticle selected (such as size or material) and on the amount of particle- or payload-loading or payload activity desired.

In preparing the treated textiles and webs of the invention, the process temperature can vary widely, depending on the affinity of the textile-reactive functional groups for the substrate.

However, the temperature should not be so high as to decompose the reactants or damage the web, or so low as to cause inhibition of the reaction or freezing of the solvent. Unless specified to the contrary, the processes described herein take place at atmospheric pressure over a temperature range from about 5°C to about 180°C, more preferably from about 10°C to about 100°C, and most preferably at "room" or "ambient" temperature ("RT"), e.g. about 20°C.

The time required for the processes herein will depend to a large extent on the temperature being used and the relative reactivities of the starting materials. Therefore, the time of exposure of the web to the polymer in solution can vary greatly, for example from about one second to about two days. Normally, the exposure time will be from about 1 to 30 seconds.

Following exposure, the treated web is dried at ambient temperature or at a temperature above ambient, up to about 90°C. The pH of the solution will be dependent on the web being treated. For example, the pH should be kept at neutral to basic when treating cotton, because cotton will degrade in acid. Additionally, the deposition of payload nanoparticles with charged groups (e.g., amines, carboxylates, and the like) is expected to be dependent on solution pH. Salts (such as, for example, NaCl) may optionally be added to increase the rate of adsorption of anionic and cationic payload nanoparticles onto the web fibers. Unless otherwise specified, the process times and conditions are intended to be approximate.

In order to further illustrate the present invention and advantages thereof, the following examples are given, it being understood that the same are intended only as illustrative and are not in any way limiting.

30

EXAMPLES

I. Textile-Reactive Anti-Biologic Beads

Fabric treatments endowing bio-activity such as anti-microbial, anti-fungal, and anti-bacterial properties are highly desired by the apparel, home furnishings, and medical industries. No natural fibers (and many other fibers under normal use conditions) can last indefinitely. Most are subject to attack by micro-organisms. When knitted or woven into fabric

and used as apparel or home furnishings materials, the fibers are in contact with human skin. Microbial, fungal, or bacterial contamination remains a priority issue. Certain fabrics are slated for hospital or other sterile applications where decontamination is of utmost importance. It is also desirable for sheets, towels, undergarments, socks, hosiery, active wear, home and institutional furnishings including carpets, and uniforms to possess anti-microbial, anti-fungal, and anti-bacterial properties.

Thus, in one embodiment of the invention, the nanobead encloses an anti-biologic agent as the payload. The resulting encapsulated anti-biologic agent preparations or nanoparticles have improved retention within and on the textile or web fiber structure.

Because the anti-biologic compounds themselves are not chemically modified, the bioactivity of the bioactive agent is not reduced or lost. The term "anti-biologic agent" as used herein and in the appended claims refers to agents or drugs having bioactivity, such as anti-microbial, anti-fungal, or anti-bacterial activity, such as 3-(trimethoxysilyl)-propyloctadecyltrimethyl ammonium chloride, known as Sylgard®. A plethora of active agents have been identified, including silver nitrate, colloidal silver, 6-acetoxy-2,4-dimethyl-m-dioxane, 2-bromo-2-nitropropane-1,3-diol, 4,4-dimethyloxazolidine, hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine, zinc dimethyldithiocarbamate, zinc 2-mercaptopbenzothiazole, zinc 2-pyridinethiol-1-oxide, N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide, to name a few as examples. See, e.g., *Sanford's Guide to Antimicrobial Therapy*, Medical Book System, 1997.

The textile-reactive anti-biologic nanoparticle of the invention is designed so that the bioactive agent is embedded or entrapped within the polymeric shell or matrix of the nanoparticle but is also able to be released from the nanoparticle in a prolonged or otherwise controllable fashion. The release profile is programmed via the chemistry of the polymer network of the nanobead. The nanoparticle can be formulated with an almost infinite degree of designed characteristics via key structural features, such as crosslinking density, hydrophilic-hydrophobic balance of the copolymer repeat units, and the stiffness/elasticity of the polymer network (for example, the glass transition temperature). In addition, erodible nanobeads can be developed to encompass dual release mechanisms of diffusion and erosion. Because of the durability of the chemical bonds between the fibers and the functional groups of the nanoparticles, the bioactive agents are depleted only by programmed release from the particles and not from unintended detachment or release of the particles themselves from the web. In addition, the polymer matrix may be designed to respond either positively or negatively to certain environmental stimuli, thus triggering or shutting off payload release.

35 II. Textile-Reactive Dye Beads

Dye retention on fabrics is important when it is desired to retain the original shade of the garment. Covalently binding the dye itself to the fabric molecule can alleviate fading.

However, chemically reactive dyes tend to be expensive because they are synthetic, and it is very difficult to chemically modify a natural (unreactive) dye to make it reactive without changing its basic color.

Therefore, in another embodiment of the invention, the textile-reactive preparations of the invention comprise an unreactive dye as the payload surrounded by or contained within a synthetic, polymer shell that is reactive to textiles or other webs, to give textile-reactive dye beads. The polymer shell of the bead has a surface that includes functional groups for binding or attachment to the fibers of the textiles or other webs to be treated. The resulting encapsulated dye preparations or beads have improved colorfastness and retention within and on the textile or web fiber structure without changing the base color of the dye. The term "unreactive dye" as used herein refers to a dye that does not normally react chemically, via covalent bonding, with a textile or web fiber. Such dyes are commonly found within the physical adsorption and mechanical retention dye groups. In a presently preferred embodiment, the unreactive dye for use in the present invention is indigo.

The dye may be water-soluble or water-insoluble. Where the dye is insoluble, it may, in certain cases, optionally be converted to a soluble form prior to incorporation into the textile-reactive bead, for process manufacturing purposes for example. After incorporation of the converted, soluble dye and polymerization of the polymeric shell, the dye is then converted back to its insoluble form within the bead. An example of this is indigo, which is water-insoluble in its desired blue form but which can be reversibly reduced to its soluble form (leuco indigo, which is yellow in color).

The textile-reactive dye bead will be small enough so that it will be transparent, allowing the color of the dye to show through.

In addition, the reactive hooks can be chosen from those that bind strongly with the textile or web fibers to be dyed, to give a darkly colored fabric, or from those that are controllably degradable, to provide varying degrees of "faded" color (for example, "stone-washed" blue jeans). One method of controllably degrading the color provided by the dye beads is to choose textile-reactive functional groups that form, with the textile, bonds that can be controllably hydrolyzed via standard chemical means. The amount of fading can be controlled by the number of hydrolyzable versus non-hydrolyzable textile-reactive functional groups present on the dye bead surfaces.

In a presently preferred embodiment of the invention, the dye is indigo and the web or textile is denim. Denim is a woven fabric formed by interlacing or intermeshing cotton yarns. The direction of weaving is called the "warp" direction, and the cross direction is called the "weft" or the "filling" or the "fill". The weft yarns alternately go over and under the warp yarns; for example, in a plain weave or a two-by-one (2X1) twill weave construction. The warp yarn in denim has been dyed with indigo, a naturally occurring blue dye, to various desired depths of

shade, from light blue to very dark blue or even black, prior to weaving. The pattern produced by weaving indigo-dyed warp yarn with white fill yarn results in the typical denim look.

Because indigo in its oxidized (blue) form is water-insoluble, the current methods for dyeing warp yarns for processing into denim fabric are cumbersome, time-consuming, and produce much waste material that must be disposed of. Additionally, for denim having a stone-washed appearance, a complicated process of enzyme digestion and/or stonewashing (optionally using bleaching agents) is currently required, which weakens both the warp and the fill yarns. Because the indigo is particulate and naturally occurring, it does not bind chemically with, nor is it otherwise permanently incorporated into, the cotton fibers of the warp yarns, so that fading of the denim quickly occurs. While this has in the past been fashionably desirable, current fashion trends call for a dark blue, nonfading denim material.

The present invention provides distinct advantages over the current process for the manufacture of denim. There is no need to perform a redox reaction on indigo during the dyeing process, with its attendant wastewater and slurry to dispose of. The present method is an easy, "one-dip" process. The textile-reactive indigo beads bind strongly with the cotton fibers to provide a dark blue fabric that does not fade. For fabric with a stone-washed appearance, fading can be achieved by a lighter dyeing without enzyme digestion. In addition, the amount of fading can be controlled by the number of degradable textile-reactive functional groups present on the indigo dye beads, by the amount of hydrolysis of the degradable beads, and/or by the size of the bead. Alternatively, the hooks on the beads will first not be allowed to react with the cotton before the garment is stonewashed to achieve the desired faded look. Upon achieving the particular faded appearance, the hooks are allowed to react with the cotton, thus freezing the look permanently in place.

While the above discussion has been directed to indigo dye and denim fabrics, the advantages of the textile-reactive beads of the present invention can be extended to other dyes and to other webs.

III. UV-Protective Textile-Reactive Beads

The harmful effects of solar radiation are well known. Ultraviolet (UV) light can cause sunburn, skin aging, premature wrinkling, and cancer. In addition, UV light is also known to fade and weaken garments and other textiles and webs.

Thus, in yet another embodiment, the textile-reactive preparations of the invention comprise a particulate sunblock agent as the payload surrounded by or contained within a synthetic, organic layer that is reactive to textiles and other webs to give textile-reactive UV-protective beads. The organic layer or shell of the bead has a surface that includes functional groups for binding or attachment to the fibers of the textiles or other webs to be treated or, alternatively, the surface includes functional groups that can bind to a linker molecule that will

in turn bind or attach the bead to the fiber. The resulting encapsulated UV-blocking preparations or beads have improved retention within and/or on the textile or other web fiber structure.

The term "particulate sunblock agent" as used herein refers to the solid physical sunblocks such as titanium dioxide, zinc oxide, silica, iron oxide, and the like, which provide a sunscreening or protective benefit through reflecting, scattering, or absorbing harmful UV or visible radiation. In a presently preferred embodiment, the particulate sunblock agent is selected from titanium dioxide and zinc oxide. Particles of TiO₂ as small as 20 nm give a material that is completely transparent in the visible range but will block UV light. Somewhat larger particles (30 – 35 nm) will start to give the material they are dispersed in some cloudiness because of the distribution of particle sizes in the commercial mixture. Larger particles produce a white color. The titanium dioxide may be used either with or without a protective inorganic coating on the particles, such as silica, alumina, zirconia, a mixture of these coatings, or other inorganic coatings. Such compositions are known in the art. Such 10 coatings prevent the production of free radicals on the surface of the TiO₂ particle upon sun exposure, and thus prevent damage to the polymer shell of the bead of the invention. Thus, when the barrier textile is to be exposed to significant amounts of light, the titanium dioxide used in the textile-reactive UV-protective bead will preferably be coated with an inorganic 15 material prior to its incorporation into the bead.

The particulate sunblock agent may be coated with silane coupling agents or it may be encapsulated with polymers to provide an organic layer surrounding the particulate. The monomeric or polymeric layer may be covalently attached to the sunblock agent particle or it may be crosslinked to form a polymeric shell around the particle. The monomers or polymers of the organic coating layer will contain a desired functionality, such as chemical "hooks" that are available to bind to a web surface.

One type of coating that may be polymeric or monomeric is formed with the silane coupling agents having the general formula R₁SiX₃, R₁R₂SiX₂, R₁R₂R₃SiX, where R₁, R₂, and R₃ are carbon-containing radicals that include a desired functionality, such as chemical "hooks" that would bind to a fabric surface. X is a hydrolyzable group that includes, but is not limited to Cl, Br, I, -OCH₃ (methoxy), -OCH₂CH₃ (ethoxy), -OR' (alkoxy, where R' is any alkyl group), -OC(O)CH₃ (acetoxyl), CH₃C=CH₂O- (enoxy), (C₂H₅)(CH₃)C=NO- (oxime), and (CH₃)₂N- (amine). These reagents have the ability to bind directly to silica and some other inorganic surfaces, such as the inorganic coating on silica-coated TiO₂ particles, as well as to react with each other to produce durable coatings. In the case of R₁R₂R₃SiX on silica, one only obtains a 30 covalent bond directly to the surface by reaction with a surface silanol group. In other words, R₁R₂R₃SiX and a HO-Si-particle react to form a R₁R₂R₃Si-O-Si-particle and no further crosslinking to other silane molecules is possible. In the case of R₁SiX₃ and R₁R₂SiX₂, one can 35

obtain bonds to the surface of the particle and bonds to other identical silane molecules to form a polymeric chain or network. The presently preferred embodiment is R_3SiX_3 because of its ability to crosslink and the greater stability it should give to a coating, followed by $R_1R_2SiX_2$ and finally $R_1R_2R_3SiX$. However, there may be applications where it is advantageous to include different silanes having different numbers of R and X groups, or silanes that have different R groups but the same number of X groups. Additionally, silane coupling agents can form durable polymeric coatings without actually covalently binding to a surface. In the case of silica, i.e., TiO_2 coated with silica, covalent bonds are expected. However, in the case of ZnO , no covalent bonds to the surface may be obtained, but a durable crosslinked coating is still attainable.

The organic layer or shell will be thin enough so that it will be essentially transparent, allowing UV light to come into contact with and be reflected, refracted, or absorbed by the sunblock agent particles. Preferably, the bead shell will be a polymer monolayer or multilayer, more preferably a monolayer.

The size of the sunblock agent particles in the sunscreening beads can be quite small, in the range of about 10 nm to about 150 nm, particularly when it is desirable for the beads to be transparent, such as when one wishes the color of the web to show through. Alternatively, if it is desirable for the web to have a white or opaque white color, larger-sized particles, generally in the range of about 100 nm to about 1000 nm, are used. Because the sunblock agent particles are protected within the polymer bead and the bead is permanently attached to the textile, there is an added benefit that the resultant color of the textile will not yellow with age or after multiple washings.

If a silane coupling agent is applied to the surface of a particulate sunblock agent, one of a number of methods that are described in the literature may be used. These include refluxing a mixture of a silane in an organic solvent with the particulate sunblock agent. An additional method that may be used is to deposit the silane from a solution of an alcohol, or a solution of water, or a solution of an alcohol and water. Bulk deposition by spray-on of a solution of the silane in alcohol onto sunblock agent particles in a high intensity solid mixer may also be utilized. Silanes that are commercially available and that contain the necessary functional groups to both bind to an inorganic surface, crosslink to itself, and bind to fabrics include 3-(triethoxysilyl)propylsuccinic anhydride (possibly employing a catalyst that is capable of reforming any opened anhydride groups) and N-(3-triethoxysilylpropyl)gluconamide (using a compound that contains two or more N-methylol groups).

To apply a polymeric coating to encapsulate the particles, the particulate material may be added to an aqueous solution of poly(ethylenimine) (PEI). It has been shown that this polymer has a high affinity for silica surfaces and other surfaces. To increase the surface coverage of PEI, excess PEI may be added to the solution, which is removed by washing the

particles after adsorption has taken place. Alternatively, a stoichiometric amount of PEI may be added so that the next reactant (a maleic anhydride-containing polymer) may be added without washing the particles. To PEI-coated beads is added a maleic acid polymer or copolymer that contains maleic acid. It is believed that the maleic anhydride polymer will react with amine groups in the PEI, binding together PEI chains, encapsulating the particles, and leaving enough free maleic anhydride or maleic acid residues on the surface of the particles to react with hydroxyl or amine groups in a textile or other web.

5 The silane-layering and polymer encapsulation methods could also be combined. For example, a silane that contains amines such as aminopropyltriethoxysilane may be added to the surface of the sunblock agent particles and a maleic anhydride-containing polymer is then 10 added to and crosslinked around these beads.

IV. Fragrances/Scents

It may be desirable to have a particular fragrance or scent impregnated into a finished 15 good, such as an article of clothing such that the fragrance can be controllably released over time. Thus, in a further embodiment of the invention, a textile-reactive nanoparticle encloses a fragrance or a scent as the payload. The nanoparticle can be designed, for example, to release the fragrance at a constant or prolonged rate or to release the fragrance in response to a particular environmental trigger such as temperature or light.

20 In one example, 3g of bisphenol A are dissolved in 10g of a solvent mixture of acetone and methylene chloride (1:3 by weight). The resulting solution is added to 30g of citronellol (an oily fragrance with a fresh, rich, rose-like scent) as the core material to form a primary solution. Thereafter, 4g of tolylene diisocyanate and 0.05g of dibutyltin laurate as a catalyst are added to the solution to form a secondary solution. These solutions are prepared at temperatures 25 lower than 25°C.

The secondary solution prepared above is slowly added with vigorous stirring to a 30 solution of 5g of acacia (gum arabic) in 20g of water, whereby an oil drop-in-water-type emulsion having oil drops of 5-10 microns in average size is formed. In this case, the above procedure is conducted while cooling the vessel so that the temperature of the system is not increased over 20°C. If the temperature of the system during the emulsification is higher than the boiling point of methylene chloride, i.e. 40°C, capsulation would begin to give capsules having uneven sizes.

When emulsification is finished, 100g of water at 40°C is added to the emulsion with stirring. Thereafter, the temperature of the system is gradually increased to 90°C over a period 35 of 30 minutes. The system is maintained at 90°C for 20 minutes with stirring to complete the capsulation. Microcapsules containing citronellol with a carbohydrate shell (acacia) are formed.

The microcapsules are attached to cotton fabric using well-known methylol chemistry to link the carbohydrate shell of the microcapsule to the cotton. DMDHEU is added to the solution to 8% by weight, followed by addition of MgCl₂ to 2% by weight of solution. 10-oz. cotton cloth is padded with this solution to 70% wet pickup and cured at 165°C for 2 minutes to covalently link the fragrance-laden beads to the fabric.

5

Examples of Other Agents That May be Used as a Payload

- V. Colloidal Pigments/Reflectors
- VI. Metallic Particles for EMF Shielding/Conductivity/Antistatic Use
- 10 VII. Thermotropic Liquid Crystals – change color based on body heat
- VIII. Magnetic Particles – used in hard disk magnetic data storage media
 - To make fabric that can be magnetized (in whole or selected spots). In the future, "patterned" magnetic/conductive regions will protect clothes from being shoplifted. There will be no need for attaching a bulky ink-filled cartridge or bulky cartridges that trigger alarm sensors at checkout counters. Also, SKU's (barcodes) can be better inventoried.
- 15 IX. Insect Repellents
- X. UV-Absorber Dyes (not particles)
- XI. Photochromic Dyes and Photoimageable Dyes
 - Useful to create patterns by imaging, rather than by printing.

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WHAT IS CLAIMED IS:

1. A nanobead comprising a payload entrapped within a polymer shell, the polymer shell comprising at least one textile-reactive functional group on its surface for attaching to a textile fiber.
5
2. A nanobead according to claim 1 wherein the polymer shell exhibits controlled release of the payload.
- 10 3. A nanobead according to claim 1 wherein the payload is selected from the group consisting of bioactive agents, anti-biologic agents, drugs, pharmaceuticals, sunblock agents, dyes, pigments, scents, fragrances, insect repellents, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, thermochromic materials, heat-absorbing or heat-releasing phase change agents, fabric softeners, zeolites, and activated carbon.
- 15 4. A nanobead according to claim 1 wherein the polymer shell is transparent or translucent.
5. A nanobead according to claim 4 wherein the payload is selected from the group consisting of a dye, a sunblock agent, and a metallic reflector colloid.
20
6. A nanobead according to claim 4 wherein the payload is an unreactive dye.
7. A nanobead according to claim 6 wherein the unreactive dye is indigo.
- 25 8. A method for synthesizing a textile-reactive payload nanobead, the method comprising: contacting a payload with a polymeric set, the polymeric set including textile-reactive functional groups, and polymerizing the polymeric set, to give a textile-reactive payload nanobead comprising a payload entrapped within a polymer shell, the polymer shell comprising at least one textile-reactive functional group on its surface for attaching to a textile fiber.
30
9. A method according to claim 8 wherein the polymeric set further comprises crosslinking agents.

10. A web comprising payload nanobeads, the payload nanobead comprising a payload entrapped within a polymer shell and being substantially permanently attached to the fiber of the web by at least one textile-reactive functional group on the surface of the polymer shell.

5 11. A web according to claim 10 wherein the payload is selected from the group consisting of bioactive agents, anti-biologic agents, drugs, pharmaceuticals, sunblock agents, dyes, pigments, scents, fragrances, insect repellents, fire retardant or suppressant chemicals, metallic reflector colloids, magnetic particles, thermochromic materials, heat-absorbing or heat-releasing phase change agents, fabric softeners, zeolites, and activated carbon; and the web
10 exhibits a greatly improved retention of the payload and its activity.

12. A web according to claim 10 wherein the payload is a dye and the web exhibits a greatly improved colorfastness and resistance to fading.

15 13. A web according to claim 10 which is denim fabric and wherein the payload is indigo dye.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/US 00/40428

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06M23/12 D06P1/22 D06P1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06M D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 665 107 A (MICALE FORTUNATO J) 12 May 1987 (1987-05-12) column 5, line 45 -column 10, line 40; claims —	1,3,5,6, 10-12
A	US 5 185 169 A (YAMAMOTO TOHRU) 9 February 1993 (1993-02-09) the whole document —	1,8-10 —/—

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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